

**Temperature effect on silicate melt-sulfide-metal trace element partitioning in the presence of sulfur under reduced conditions.** B. A. Anzures<sup>1,2</sup>, K. E. Vander Kaaden<sup>3</sup>, F. M. McCubbin<sup>2</sup>, K. Iacobino<sup>4</sup>, K. Prissel<sup>4</sup>, M. Righter<sup>5</sup>, K. Righter<sup>2</sup>, A. Lanzirotti<sup>6</sup>, M. Newville<sup>6</sup>. <sup>1</sup>Lunar and Planetary Institute/USRA. <sup>2</sup>ARES, NASA Johnson Space Center. <sup>3</sup>NASA Headquarters. <sup>4</sup>Jacobs JETS, NASA Johnson Space Center. <sup>5</sup>Dept. Earth & Atmospheric Sciences, University of Houston. <sup>6</sup>Center for Advanced Radiation Sources, University of Chicago, Email: brendan.a.anzures@nasa.gov

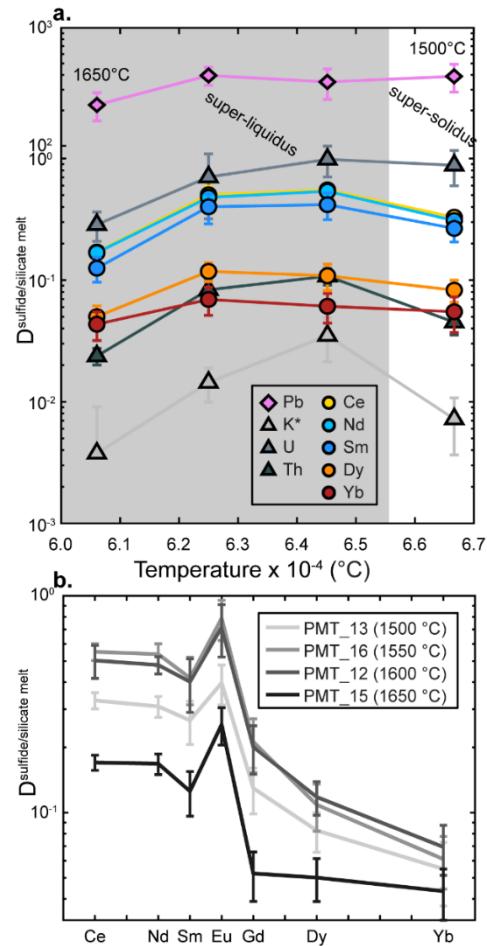
**Introduction:** The reduced nature of Mercury, enstatite chondrites, and the aubrite parent bodies (APB) have raised many questions regarding the geochemical behavior of typically lithophile, heat-producing, and rare-earth elements (REE) in magmas at low oxygen fugacity ( $f\text{O}_2$ ). Due to decreasing O availability at these low  $f\text{O}_2$ , and an abundance of  $\text{S}^{2-}$ , sulfur (S) acts as an important anion that changes the partitioning behavior of many elements and modifies the physical properties of silicate melts. Preliminary observations suggest that major and minor elements exhibit different geochemical affinities in highly reduced, S-rich systems compared to terrestrial rocks [1-6]. The speciation and bonding environment of S, dictated by P/T/ $f\text{O}_2$  conditions, may strongly influence the degree to which S affects partitioning behavior.

Here we investigate the partitioning behavior of major, minor, and trace elements between silicate melt, sulfide melt, and metal as well as the coordination chemistry of S in highly reduced silicate melts. Our work is focused on investigating solely the entropy-dependent temperature effect on partitioning of elements for which we currently have MESSENGER data (K, Na, Th, U, Si, Mg, Fe, Ti, Ca, Al, Cr, Mn, S, Cl) as well as a host of geochemically relevant trace elements such as REEs (P, Co, Ni, Mo, Ce, Nd, Sm, Eu, Gd, Dy, Yb). Previous studies in which temperature, pressure, and  $f\text{O}_2$  were co-varied found that as  $f\text{O}_2$  decreases, heat-producing elements U and Th become more chalcophile, while K becomes less chalcophile [1-4]. Concurrently, nominally lithophile elements Mg and Ca become more chalcophile and were observed as minor elements in exsolved sulfides [7] and bonded with S species in silicate melt [8]. These studies, however, could not disentangle entropic effects from changes in the  $f\text{O}_2$ . New temperature-dependent partitioning data from our work will be used to determine which elements are most likely to retain their lithophile character and hence be incorporated into silicates, and which elements are likely contained within the sulfide (chalcophile) and metal core (siderophile), setting the stage for the thermal and magmatic evolution of reduced planetary bodies.

**Methods:** Experimental samples of silicate melt, iron sulfide, iron-silicon metal, and silicon metal consistent with a predicted mercurian mantle and core composition were prepared in a piston cylinder at NASA Johnson Space Center (JSC). Experiments were conducted at 1 GPa at temperatures of 1500 to 1650 °C.

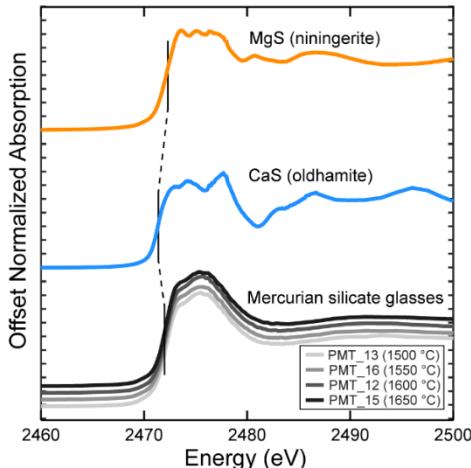
$f\text{O}_2$  was controlled by varying the Si content of the initial metal (e.g. 95:5 and 90:10 Fe:Si in wt.%). Major element compositions of silicate melt, sulfide, and metal were measured using the JEOL 8530 field emission electron microprobe (EPMA) at NASA JSC.

Trace element compositions including REEs, K, U, Th, and Pb were measured by Laser Ablation Inductively Coupled Mass Spectrometry (LA-ICP-MS)



**Figure 1.** Sulfide-silicate partition coefficients vs. a) temperature and b) rare-earth elements. \*K partition coefficients calculated from EPMA rather than LA-ICP-MS data.

using the 193 nm wavelength PhotonMachine Excite coupled to a Analytik Jena quadrupole ICP-MS at the University of Houston (laser fluence of  $\sim 3.95 \text{ J/cm}^2$  at 35% laser energy, 10 Hz and spot size of 20–50  $\mu\text{m}$ ). Uncertainties were calculated as propagated 1  $\sigma$  weighted mean error.



**Figure 2.** *S K-edge XANES spectra of silicate glass from Mercurian temperature series experiments (1500 – 1650 °C) along with MgS and CaS standards.*

Sulfur and chromium speciation in silicate melt were measured using S K-edge and Cr K-edge X-ray Absorption Near Edge Structure (XANES) spectra collected in a helium environment using an undulator-based, hard, X-ray microprobe at Argonne National Laboratory. The spot size was 2  $\mu\text{m}$  with a nominal penetration depth of 2–3  $\mu\text{m}$  for S and 10  $\mu\text{m}$  for Cr. XANES spectra were normalized using an automated edge-step normalization algorithm. Quantification of S speciation in the silicate glass spectra into their component pure sulfide spectra was completed by linearly unmixing minimizing root mean squared error and maximizing  $r^2$ , keeping in mind chemical constraints as described in [8].

**Trace Element Results:** Trace element results show that REEs, K, U, Th, and Pb are more chalcophile than siderophile, with metal trace element concentrations largely below the detection limit unlike sulfide and silicate melt, which are consistent with previous experiments at similarly reducing conditions [1-6]. However, unlike Wohlers & Wood (2017)'s [3] 1.5 GPa experiments that show a positive effect on chalcophile behavior for these elements with increasing temperature, we observe decreasing sulfide-silicate partition coefficients for REEs, K, U, Th, and Pb for super-liquidus 1 GPa experiments from a narrow temperature range of 1550 to 1650 °C as shown in **Figure 1**. Additional experiments will assess whether these conflicting results could be kinetically driven, as the experiments of [3] were run for 10–60 minutes and ours for 2–8 hours.

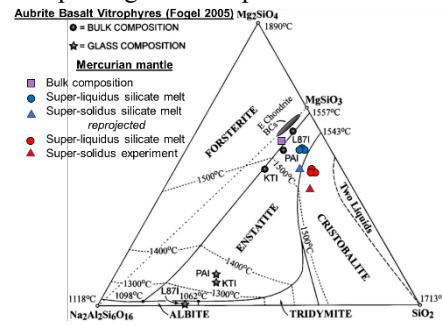
**S Speciation Results:** Unlike oxygen fugacity, pressure, and composition [8,9], temperature appears to have a negligible effect between X and X °C on sulfide speciation under very reducing conditions as revealed by S XANES spectral unmixing. Super-solidus experiment at 1500 °C and super-liquidus experiments

from 1550 to 1650 °C have consistent S speciation at  $(\text{Mg}_{80}\text{Ca}_{20})\text{S}$  within 1  $\sigma$  standard error of 10% as shown in **Figure 2**. This is consistent with another super-solidus temperature series using mercurian Borealis Plantatia composition from 1310 to 1500 °C within a limited range of  $f\text{O}_2$  (IW-5.8 to IW-6.8) and lower pressure (0.1 GPa) [9]. Temperature does, however, increase sulfur solubility in very reduced silicate melts [e.g. 10].

**Implications:** In contrast with [1]’s much shorter run durations, our preliminary experiments show a generally negative effect on rare earth element and heat-producing element partitioning with increasing temperature, although more experiments are needed to expand this T range and assess steady state behavior.

New S speciation results can be used to re-project silicate ternaries by apportioning Mg and Ca to bond with S and O. In a forsterite-albite-silica ternary using  $(\text{Mg}_{80}\text{Ca}_{20})\text{S}$  as the S speciation in the silicate melt, silicate compositions would push phase stability away from forsterite and toward silica, as well as compositions away from anorthite and towards albite as shown in **Figure 3** [11]. For enstatite chondrite and aubrite meteorites, Fogel (2005) assumed all S dissolved in the silicate melt would bond with Ca. Correcting the re-projection with current S speciation results pushes aubrite basalt vitrophyre compositions away from albite towards tridymite, consistent with the relative abundance of silica polymorphs in aubrites and enstatite chondrites. For Mercury's mantle, this could allow silicate phase proportions to be calculated from existing S-poor and oxidized systems, provided they are similarly Fe-poor.

Melt speciation will also be further investigated by measuring Cr and Cl XANES spectra. These particular heterovalent elements are important because at low  $f\text{O}_2$  various cations (e.g. Fe, Ca, Mg, Na, K) may bond with S, Cl, and Cr rather than just O, impacting metal and sulfide complexing and transport.



**Figure 3.** Forsterite-albite-silica phase diagram annotated from [11]. Mercurian lava compositions are reprojected in red taking into account  $S$  bonding with  $Mg$  and  $Ca$  as  $Mg_{80}Ca_{20}$ .

**References:** [1] McCubbin et al. (2012) *GRL*, **39**, 9. [2] Vander Kaaden et al. (2016) *GCA*, **173**, 246-263. [3] Wohlers & Wood (2017) *GCA*, **205**, 226-244. [4] Boujibar et al. (2019)

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